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Recent Developments in the Ring-Opening Polymerization of ε-Caprolactone and Derivatives Initiated by Tin(IV) Alkoxides

*Ph. Lecomte, F. Stassin, R. Jérôme**

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6a, 4000 Liège, Belgium
E-mail: rjerome@ulg.ac.be; http://www.ulg.ac.be/cerm

Summary: The macromolecular engineering of aliphatic polyesters by ring-opening polymerization (ROP) initiated by aluminum alkoxides is now well established. Tin (IV) alkoxides are less popular, mainly because of a poorer control of the chain growth. This paper discusses some recent examples from CERM, showing that tin (IV) alkoxides can advantageously replace the aluminum counterparts as ROP initiators. For instance, they can initiate successfully the Ring-Opening Polymerization of α-chloro-ε-caprolactone and dioxepane-2-one. They are also very promising initiators for ROP in supercritical CO_2 and for the synthesis of clay/aliphatic polyester nanocomposites.

Keywords : nanocomposites; polyesters; ring-opening polymerization; supercritical carbon dioxide; tin alkoxides

Introduction

Due to the remarkable properties of biodegradability and biocompatibility, aliphatic polyesters are very promising either as biomaterials or as environmentally friendly materials to address growing ecological concerns.[1,2] During the last decades, ring-opening polymerization (ROP) of lactones and lactides has proven to be a powerful tool to produce high molecular weight aliphatic polyesters. When ROP is initiated by suitable organometallic species, i.e., metal alkoxides with d-orbitals of a favourable energy, irreversible termination and transfer reactions are negligible, and ROP turns living. Many examples are known in which the polymer molecular weight is predetermined by the monomer to initiator molar ratio and the concentration in propagating species is constant. Moreover, the chemical structure of the chain-ends can be controlled, and the

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polymerization of a second monomer by a living polyester can be initiated with formation of block copolymer. Whenever the initiation step is fast compared to propagation, a low polydispersity index ($M_w/M_n \approx 1.1$) is reported. Nowadays, real macromolecular engineering is carried out as witnessed by a steadily increasing number of papers reporting on the synthesis of diblock, triblock, star-shaped, graft, hyperbranched and dendritic polyesters.[2]

Aluminum alkoxides are very popular ROP initiators because of the very efficient control of the molecular weight parameters.[2] The polymerization proceeds through the well-known "coordination-insertion" mechanism. Polydispersity is low, and transesterification reactions are not significant (kinetic control) until the quasi complete conversion of the monomer. Although tin (IV) alkoxides are easily available, their use has been limited for a long time, because of less efficiently controlled polymerization. In this respect, Penczek et al. reported that selectivity of propagation versus transesterification was lower with tin(IV) than with aluminum alkoxides.[3] Among possible reasons, Kricheldorf et al. proposed slow initiation, possible equilibrium between aggregated/unaggregated species and occurrence of transesterification reactions.[4]

This paper reports on particular examples in which tin(IV) alkoxides are more attractive than their aluminum counterparts, despite a poorer control. The first part is devoted to the polymerization of ε-caprolactone (εCL) derivatives substituted by functional groups. ROP in supercritical carbon dioxide is the topic of the second part. Finally, special attention is paid to the production of PCL nanocomposites, by polymerization in the presence of nanofillers, in both organic media and supercritical CO_2.

Synthesis of poly(ε-caprolactone)s with pendent functional groups

There are two major reasons for attaching functional groups to polyester chains. Firstly, it is highly desirable to tune important properties, such as crystallinity, hydrophilicity, biodegradation rate, bioadhesion, etc. Moreover, functional groups may be used to attach active molecules, e.g., drug, recognition agent, adhesion promoter, probe, etc. Synthesis and polymerization of lactones substituted by a functional group is a straightforward route to new aliphatic polyesters. Figure 1 shows a series of substituted-ε-caprolactones that have been successfully synthesized and polymerized by aluminum alkoxides.[5-22]

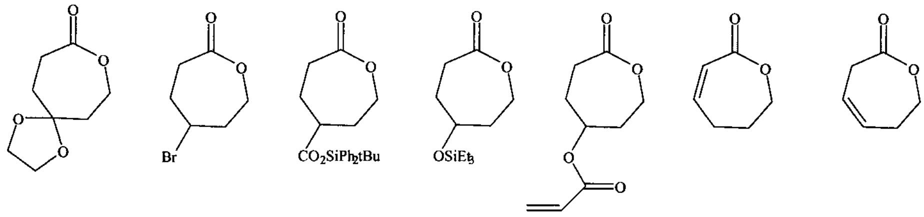

Figure 1. Substituted ε-caprolactones polymerizable by $Al(OiPr)_3$

Synthesis of copolymers of oxepane-1,5-dione and ε-caprolactone

Poly(oxepane-1,5-dione) (POPD) is a highly crystalline polymer, which exhibits a high T_m (147°C) and a T_g of 37°C.[23,24] Both PCL and POPD have an orthorombic unit cell. Remarkably, poly(OPD-co-εCL) random copolymers show a linear increase of T_m with the molar content of OPD units, as a consequence of the isomorphism of PCL and POPD (Figure 2). To the best of our knowledge, this behavior has never been reported before for aliphatic polyesters. It is remarkable that only 30 mol% oxepane-1,5-dione (OPD) copolymerized with εCL is sufficient to increase T_m from 60°C up to 90°C, which opens up new applications, e.g., in the packaging field. The hydrolytic and thermal behavior of these copolymers has been reported elsewhere.[25]

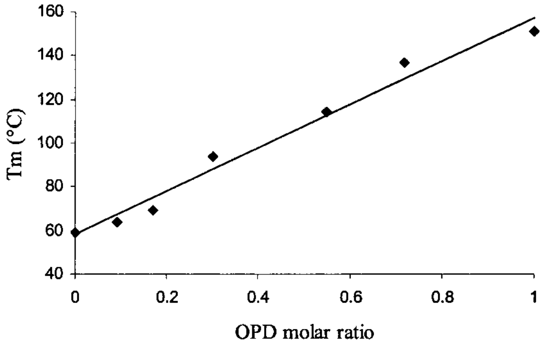

Figure 2. Dependence of the T_m of poly(OPD-*co*-εCL) with the OPD molar ratio

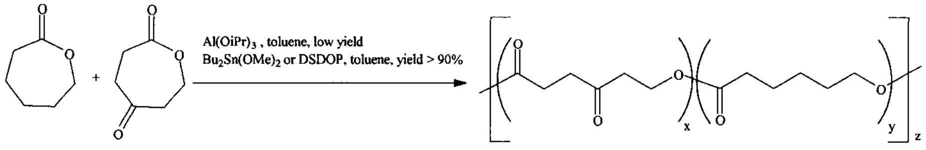

Figure 3. Copolymerization of OPD and εCL into poly(OPD-co-εCL)

Aluminum alkoxides are not proper initiators for copolymerization of OPD and εCL, because they do not tolerate the ketone group (Figure 3).[24] Table 1 shows indeed that the reaction of εCL with aluminum isopropoxide is perturbed by cylcohexanone as soon as the $[\text{cyclohexanone}]_0$ / $[\text{Al(OiPr)}_3]_0$ molar ratio is 20 and higher, as assessed by exceedingly high M_n and polydispersity. As a rule, the yield of the OPD/εCL copolymerization is very low when Al(OiPr)_3 is used as an initiator (Figure 3, Table 2). The reason for this disappointing observation is the preferential complexation of Al to the carbonyl group of the ketone rather than to the one of the lactone, which is detrimental to ROP of the monomer.

Table 1. Influence of the $[\text{cyclohexanone}]_0$ / $[\text{Al(OiPr)}_3]_0$ molar ratio on the εCL ROP

Entry	$[\text{Cyclohexanone}]_0$ / $[\text{Al(OiPr)}_3]_0$ [a]	Yield (%)	M_n [b]	M_w / M_n
1	0	86	10.5 K	1.3
2	2	88	10 K	1.3
3	20	80	18 K	1.3
4	200	45	400	2.8

(a) conditions : [εCL] = 0.9M, toluene, room temperature, M_n,th at complete conversion = 12 K.
(b) PMMA calibration.

Table 2. Bulk copolymerization of εCL and OPD (f_{OPD}=0.3)

Entry	Initiator	$[M]_0/[In]_0$	f_{OPD}	Time	Yield	F_{OPD}	M_n (SEC) [c]	M_w/M_n
1	$Al(OiPr)_3$ [a]	400	0.05	24 h	4 %	-	-	-
2	$Al(OiPr)_3$ [a]	400	0.05	1 week	38 %	0.01	7 K	1.3
3	$Bu_2Sn(OMe)_2$ [b]	300	0.3	3 min	97 %	0.27	21 K	2.1
4	$Bu_2Sn(OMe)_2$ [b]	600	0.3	5 min	95 %	0.31	39 K	1.9
5	DSDOP [b]	300	0.3	3 min	92 %	0.31	40 K	1.6
6	DSDOP [b]	600	0.3	5 min	94 %	0.31	65 K	1.6

(a) conditions: toluene, 90°C, [M]=2M. (b) bulk, 110°C. (c) PMMA calibration

Substitution of dibutyltin dimethoxide for aluminum isopropoxide is an efficient strategy to solve this problem. Table 3 shows that cyclohexanone no longer has a detrimental effect on the εCL polymerization. High yields of poly(OPD-co-CL) are obtained when ROP is initiated by tin(IV) alkoxides, such as dibutyltin dimethoxide and 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) (Table 2).

Table 3. Influence of the $[\text{cyclohexanone}]_0$ / $[Bu_2Sn(OMe)_2]_0$ molar ratio on the ROP of εCL

Entry	$[\text{Cyclohexanone}]_0$ / $[Bu_2Sn(OMe)_2]_0$ [a]	Yield (%)	M_n [b]	M_w/M_n
1	0	93	20 K	1.5
2	30	93	18 K	1.4
3	100	92	19 K	1.6
4	500	94	18 K	1.4

(a) conditions : [εCL] = 0.9M, toluene, room temperature, M_n,th at complete conversion = 22 K.
(b) PMMA calibration

Synthesis of copolymers of α-chloro-ε-caprolactone

DSDOP proved to be a very efficient initiator for ROP of αClεCL.[26] Table 4 shows that molecular weight is predetermined by the monomer to initiator molar ratio. The polydispersity (ca. 1.2) is lower than that observed for the εCL polymerization, whereas the electrowithdrawing chloro group increases the polymerization rate of αClεCL compared to εCL. Although, block and random copolymers of εCL and αClεCL can be synthesized with DSDOP, these reactions are a failure in the presence of aluminum isopropoxide.

Table 4. Ring-Opening Polymerization of αClεCL inititiated by DSDOP

Entry	$[\alpha\mathrm{Cl}\varepsilon\mathrm{CL}]_0$ / $[\mathrm{DSDOP}]_0$ [a]	Time	Yield	$M_n th$	M_n (SEC) [b]	M_w / M_n
1	16.9	90 min	100 %	2500	2500	1.4
2	33.8	90 min	100 %	5000	6000	1.3
3	67.6	10 min	89%	9000	8000	1.2

(a) Conditions: toluene, room temperature. (b) polystyrene calibration

Poly(ε-caprolactone) containing α-chlorinated units is very promising because of easy derivatization (Figure 4). Indeed, reaction of αClεCL with 1,5-diazabicyclo(4.3.0)non-5-ene (DBN) results in an unsaturated lactone, which can thereafter be polymerized into unsaturated polyester. The α-chloro esters units are initiators for atom transfer radical polymerization (ATRP). So, the radical polymerization of MMA has been initiated by a random copolymer of εCL and αClεCL with the traditional $\mathrm{CuCl/CuCl_2}$/HMTETA ATRP catalyst. Moreover, reaction of benzoyl-3-butenyl with poly(εCL-co-αClεCL) (molar fraction of αClεCL ($F_{\alpha\mathrm{Cl}\varepsilon\mathrm{CL}}$) = 0.5) at 60°C in N,N-dimethylformamide (DMF) in the presence of CuBr and tris[2-(dimethylamino)ethyl]amine ($\mathrm{Me_6TREN}$), results in the quantitative insertion of olefin by atom transfer radical addition (ATRA). This strategy is very versatile because many functional groups can be attached to the same poly(εCL-co-αClεCL) chains, merely by changing the structure of the olefin involved in the ATRA process. PCL's with pendent alcohol, carboxylic acid, amine and epoxide groups have been prepared, as will be reported in a forthcoming paper. This synthetic pathway to α-substituted PCL's is very straightforward because only three steps from commercially available materials are required, i.e., the Baeyer-Villiger oxidation of α-chlorocyclohexanone, ring-opening polymerization of αClεCL and finally ATRA of functional olefins (Figure 4).

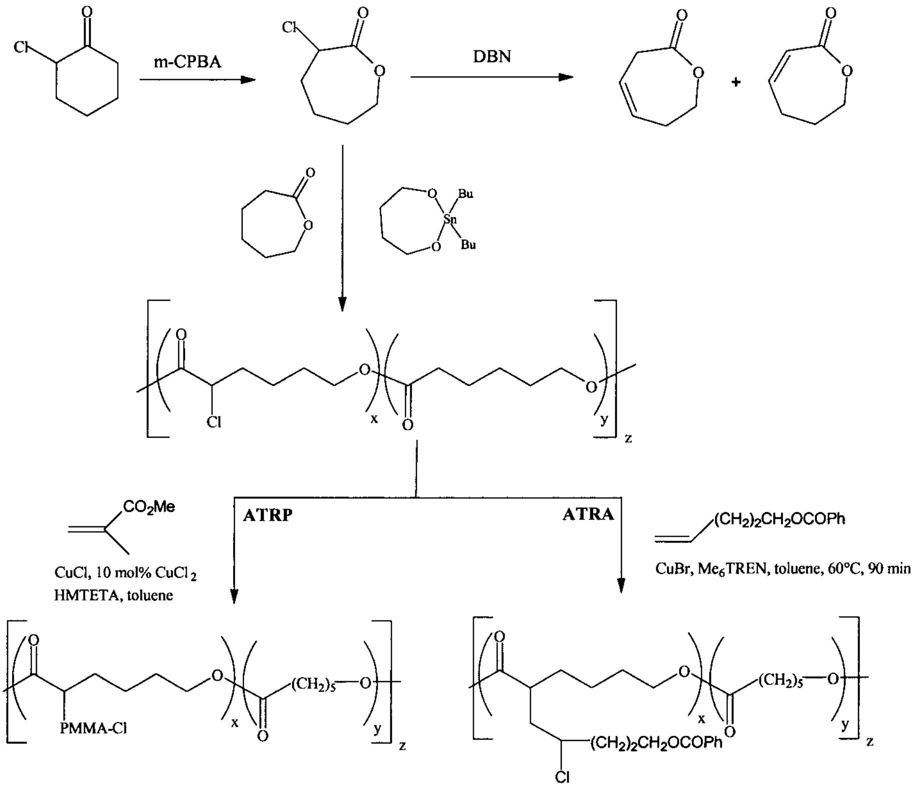

Figure 4. Synthesis and chemical transformation of poly(εCL-*co*-αClεCL) by ATRA and ATRP

Ring-Opening Polymerization of cyclic (di)esters in Supercritical CO_2

Environmental concerns have recently prompted the scientific community to investigate new ways to decrease the use of volatile organic solvents. For this purpose, the use of supercritical fluids appears to be a valuable alternative. Indeed, supercritical fluids combine gas-like and liquid-like properties (solvation power and density). Amongst available supercritical fluids, supercritical carbon dioxide is the best candidate because of low toxicity, low cost, non flammability and easily accessible critical parameters (T_c = 31.4°C, P_c = 73.8 bar). Moreover, CO_2 is widely available from commercial and industrial supplies and is also easily recycled.

Tin(IV) alkoxides are very efficient initiators for ROP of εCL in supercritical CO_2 (40°C and 210-215 bar).[27] The ^{1}H NMR analysis of the chain ends has confirmed that ROP proceeds through the coordination-insertion mechanism that commonly operates in organic solvents. When polymerization starts, the medium is transparent because the monomer and the very short PCL oligomers are soluble. After a few minutes, the medium turns cloudy as result of the precipitation of the non-soluble PCL chains. Nevertheless, the experimental molecular weight increases regularly with conversion and is predetermined by the monomer-to-initiator molar ratio, at least until 20000 g/mol (Figure 5), on the assumption that the two alkoxides are active. The first order in εCL is observed, and the first order in initiator indicates that tin species are mostly unaggregated in supercritical CO_2. This behavior is different from ROP in toluene, because then the kinetic order in initiator changes with concentration, a value of 1.3 being found at low initiator concentration. Penczek et al. proposed that a kinetic order higher than 1 would be the signature of an equilibrium between more reactive aggregated species and less reactive unaggregated species.[3] This observation is unexpected because, as far as aluminum alkoxides are concerned, unaggregated species are less reactive, which results in a kinetic order lower than 1.

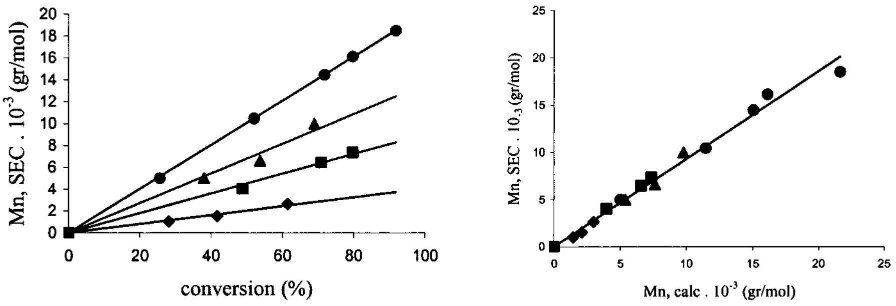

Figure 5. Dependence of M_n (SEC) on the monomer conversion and on theoretical M_n for the εCL ROP initiated by $Bu_2Sn(OMe)_2$ in supercritical CO_2. $[εCL]_0$= 1.39M, $[εCL]_0$ / $[Sn]_0$ = 364 (square), 254 (diamond), 167 (triangle), and 88 (circle)

For the sake of comparison, the apparent rate constants for ROP of εCL have been measured in different media: k_{app} is 56 x 10^{-3} min^{-1} in toluene, 130 x 10^{-3} min^{-1} in bulk, 15 x 10^{-3} min^{-1} in CFC-113 and 3.95 x 10^{-3} min^{-1} in supercritical CO_2. Thus ROP at 40°C proceeds ca. 14 times faster in toluene and 33 times faster in bulk than in supercritical CO_2. This very slow kinetics has been explained by an equilibrium between propagating species and dormant species. The reversible insertion of CO_2 into the Sn-O bond leads to a carbonated tin compound, as shown in Figure 6.[27] This mechanism has been substantiated by spectroscopy and the activation parameters for the reaction.[28]

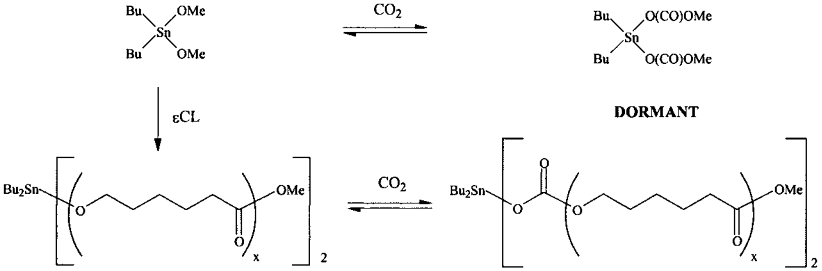

Figure 6. Reversible carbonation of propagating tin (IV) alkoxide by CO_2

When aluminum triisopropoxide is the initiator, ROP of εCL is a failure, as testified by formation of only a few percents of oligomers, as result of the high reactivity of aluminum alkoxide towards CO_2.

It is highly desirable to prepare polyesters free of tin residues in view of biomedical applications. After polymerization, tin remains chemically bonded to the polymer as an ω-alkoxytin moeity and has to be removed from the final polymer. Unreacted monomer has also to be extracted in order to provide polymer with high purity. Purification of PCL by sc CO_2 has been investigated. In a first step, εCL dissolved in the polymerization medium has been extracted by supercritical CO_2. For this purpose, the phase diagram was set up by the cloud point method. εCL exhibits a LCST/UCSP behavior typical of many supercritical CO_2 / solute systems. For instance, 20 v/v % of εCL are dissolved in supercritical CO_2 at 40 °C under a pressure of ca.100 bar, while the solubilization pressure is approximately 135 bar at 50 °C. Figure 7 shows the first-order kinetic profile for the supercritical fluid extraction (SFE) of εCL from a PCL sample containing 15 wt % of monomer. Based on the extraction constant, 95 % of εCL is extracted after ca. 110 minutes, while 99 % of extraction would require ca. 175 minutes. The extraction of tin from PCL is a more difficult task because PCL-bound tin alkoxide has first to be derivatized into species soluble in supercritical CO_2. The strategy consists of reaction of the PCL-alkoxytin end-group with acetic acid and release of dibutyltin diacetate which is extractable by supercritical CO_2. The extraction of tin has been monitored by thermogravimetry and quantified by UV-visible absorption spectrometry. The kinetic profile is quasi-linear (Figure 8) and the slope of the straight line allows the extraction constant to be determined. Extraction of tin is 2.5 times lower than extraction of εCL out of PCL.

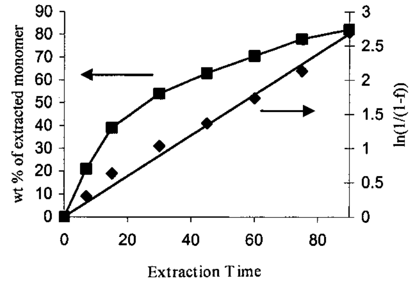

Figure 7. Kinetic profile for the extraction of CL from PCL at 40 °C and 150 bar, at a flow rate of 6 ml/min

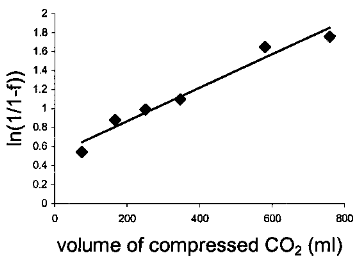

Figure 8. Kinetic profile for the extraction of dibutyltin diacetate from PCL at 40 °C and 150 bar, at a flow rate of ca. 4 ml/min

ROP of εCL in supercritical CO_2 has also been carried out in the presence of various poly(tetrahydroperfuorodecylacrylate-b-caprolactone) diblock copolymers. These surfactant contain one CO_2-philic block (PAC8) responsible for steric stabilization and one CO_2-phobic block (PCL) responsible for anchoring to the growing PCL particles. Microspheres have accordingly been prepared with [PCL(20K)-b-PAC8(40K)] surfactant. (conditions: 10 vol% CL, M_n,th = 20 k ; 5 wt% surfactant, 40°C, 300 bar, 400 rpm, 15h) as illustrated in Figure 9.

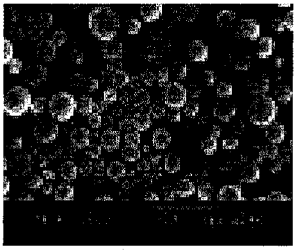

Figure 9. Preparation by of microspheres dispersion ROP of εCL in supercritical CO_2

Synthesis of nanocomposites

Dispersion of nanoclay sheets into a polymeric matrix is an efficient tool to improve properties, such as thermal stability, mechanical strength, permeability to gases and moisture and enhancement of flame retardancy as result of charring effect. PCL/clay nanocomposites are of special interest not only because of the biocompatibility and biodegradability of PCL but also because of the PCL miscibility with other polymers, including PVC.

A first preparation method for PCL/clay nanocomposites relies on the melt blending of PCL and clay, i.e. natural montmorillonite (MMT) or MMT surface modified by quaternary ammonium salts.[29,30] Moreover, PCL/clay nanocomposites have been prepared by the "in situ intercalative polymerization" process.[31,32] Bulk εCL polymerization has been promoted by dibutyltin dimethoxide in the presence of MMT either native or MMT surface modified by dimethyl 2-ethylhexyl and methyl bis(2-hydroxyethyl) ammonium cations (MMT-C_8H_{17} and MMT-$(CH_2CH_2OH)_2$).[33] The polyester chains are then growing within the clay galleries. The targeted content of filler ranged from 1 wt% up to 10 wt%. In the presence of native MMT, intercalated structures are observed in contrast to exfoliated structures, which are formed when the surface of MMT is modified by cations bearing hydroxyl groups (Figure 10). The hydroxyl groups available at the surface of MMT-$(CH_2CH_2OH)_2$ are reacted with $Bu_2Sn(OMe)_2$ and converted into tin alkoxides. As a rule, M_n decreases upon increasing the MMT-$(CH_2CH_2OH)_2$ content (Table 5, entries 2 to 4), such that the clay to monomer molar ratio allows the molecular weight to be predicted. In parallel, the polydisperisty index decreases from 1.95 down to 1.55 when the MMT-$(CH_2CH_2OH)_2$) content is increased from 1 wt% up to 10 wt% because the propagating chains are confined within the clay interlayer, which is thought to impose limitation to the mobility of the tethered chains, which are less prone to take part to transesterification reactions (Table 5). In contrast, M_n is independent of the MMT-C_8H_{17} content (Table 5, entries 5 and 6). The intercalation process has been extended to PCL nanocomposites with a high clay content (typically in the 25-50 wt% range) in order to prepare masterbatches, which can thereafter be dispersed into molten PCL or PVC, so that the final clay content is lower than 10 wt%.[34]

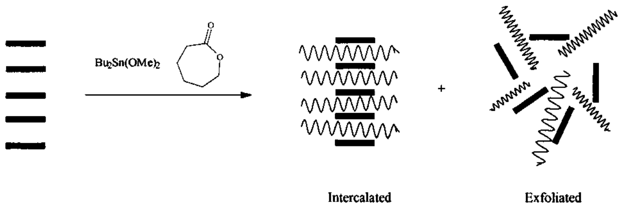

Figure 10. Intercalation/exfoliation of clays by ROP of εCL

Whenever the "in situ" intercalative polymerization is carried out in the bulk, the recovery of the material is a problem because of an exceedingly high melt viscosity. In order to tackle the problem, the polymerization in the presence of MMT has been conducted in supercritical CO_2.[32] The nanocomposite is then collected as a coarse powder. Table 6 shows that the molecular weight is in line with the theoretical value, except for the entry 2. In this case, chain transfer reaction with hydroxyl groups located at the clay surface would have occurred, so accounting for a lower M_n and a higher polydispersity. Because of the solubility of εCL and the high dispersibility of the clay in supercritical CO_2, high clay loading can be considered at least up to 50wt%.

Table 5. Bulk polymerization of εCL in the presence of MMT

Entry	MMT [a]	Filler content (wt %)	$M_{n,th}$	M_n [b] (SEC)	M_w / M_n
1	-	0	17.1 K	21 K	2.05
2	MMT-$(CH_2CH_2OH)_2$	1	13.7 K	16 K	1.95
3	MMT-$(CH_2CH_2OH)_2$	3	11.2 K	13.5 K	1.80
4	MMT-$(CH_2CH_2OH)_2$	10	5.6 K	4.5 K	1.55
5	MMT-C_8H_{17}	1	17.1 K	14.5 K	2.05
6	MMT-C_8H_{17}	5	17.1 K	17.5 K	2.05

(a) conditions: $[CL]_0/[Bu_2Sn(OMe)_2]_0 = 300$, 24h, room temperature (b) universal calibration

Table 6. Polymerization of εCL in the presence of MMT in supercritical CO_2

Entry	$M_{n,th}$	M_n (SEC) [a]	Time	Conv	M_w/M_n
1 [a]	17.8 K	15.0 K	24 h	85 %	1.65
2 [b]	40.0 K	29.0 K	24 h	100 %	1.80
3 [c]	11.3 K	13.1 K	24 h	70 %	1.60
4 [d]	40.0 K	41.0 K	24 h	100 %	1.60

(a) 4 wt % (MMT-$(CH_2CH_2OH)_2$), 50°C, 190 bar (b) 3 wt % (MMT-$(CH_2CH_2OH)_2$), 50°C, 165 bar (c) 5 wt % MMT-C_8H_{17}, 50°C, 190 bar (d) 3 wt % MMT-C_8H_{17}, 50°C, 165 bar. (e) universal calibration

Conclusions

This paper has shown that tin alkoxides are attractive initiators for the Ring-Opening Polymerization of εCL and derivatives. The efficiency of tin alkoxides has been illustrated for polymerizations in which aluminum alkoxides completely failed. The Ring-Opening Polymerization of α-chloro-ε-caprolactone and dioxepane-2-one is a representative example. Although ROP of cyclic (di)esters in supercritical carbon dioxide cannot be promoted by aluminum alkoxides, tin alkoxides proved to be successful. They have also been used to prepare nanocomposites in the presence of montmorillonite modified by methyl bis(2-hydroxyethyl-ammonium cations.

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